A

Dissertation on

Adsorptive removal of Safranin (dye) using Low Cost Adsorbent

Submitted in Partial Fulfillment for the Award of the Degree

of

Master of Technology (Chemical Engineering)

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"Adsorptive Removal of Safranin dye using low cost Adsorbent"** in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering, submitted in the Department of Chemical Engineering, National Institute of Technology, Rourkela, Odisha, is an authentic record of my own work carried out during the period of July 2012 to May 2013 under the supervision of **Dr. A. Kumar**, Assistant Professor, Department of Chemical Engineering, National Institute of Technology, Rourkela, Odisha.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

Date:

Place: Rourkela

Vivek Kumar Singh

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Date:

(**Dr. Arvind Kumar**)

Supervisor

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ABSTRACT

There is a regular industrial practice of disposing or emitting of chemical dye material to environment in the form of liquid effluent, which is a matter of global concern. Dyes are widely used in several industries like textile, dyeing, paper and pulp, tannery, paint industries etc. Dyes are considered an objectionable type of pollutant because they are toxic in nature and can be detected from bare eyes. Their classification can be done based on their usage, group and solubility. Various treatment processes used for the removal of dyes include adsorption, microbial degradation, wet air oxidation, ion exchange etc. Low cost adsorbents are available option for dyes removal from aqueous effluents. However, high cost of commercial adsorbents like activated carbon and others, material are losses during their usage, but by regeneration pose can be a best utilization of costlier adsorbent.

Adsorbent was self-prepared in laboratory from blackberry seed, which is raw biomass. The adsorbent was characterized for BET surface area, point of zero charge, CHNS, TGA, SEM, FTIR etc.

Safranin basic dye, removal from the wastewater using activated blackberry adsorbent (ABC) which was self-prepared.

Here batch studies were conducted to evaluate the effect of adsorbent dose, contact time, pH, initial concentration at 25 ^{0}C.The equilibrium adsorption data of Safranin (dye) on adsorbent were analysed by the Langmuir, Freundlich and Temkin isotherm models. The isotherm data were well described by the Langmuir isotherm model. Pseudo-first-order, pseudo-second-order models were used to analyze the kinetic data obtained at different concentrations. The adsorption kinetics was well described by the pseudo-second-order kinetic model. For Safranin-ABC system maximum adsorption capacity were found to 39.683 mg/g at 25^{0}C.Adsorption experiment has carried out to show that maximum adsorption and it observed in acidic medium for ABC.

Key words: Safranin, Point Zero Charge (pH_{pzc}), Activated Blackberry Carbon(ABC), Adsorption Isotherms, Equilibrium, Kinetics.

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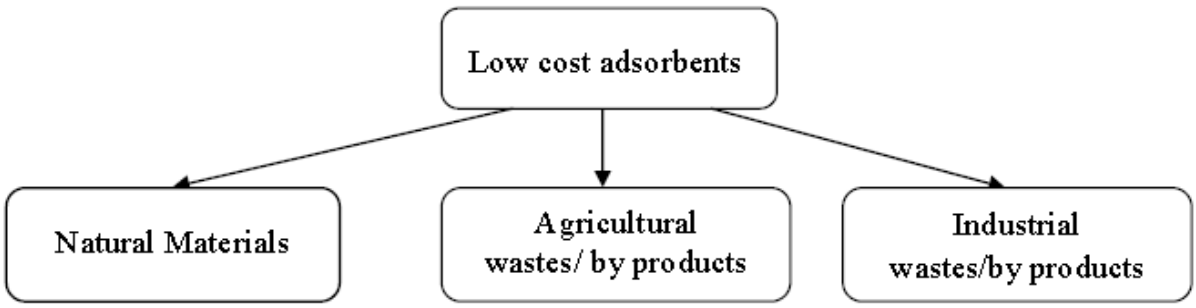
CHAPTER 1
INTRODUCTION

1. INTRODUCTION

Dyes are mostly used in various industries like textile, paper, food, plastics in order to colour their final products. It is also used in chemical as well as radiochemical laboratories for the purposes of analytical means. Waste waters disposed from different industries and from many biological laboratories are polluted by dyes. Due to the presence of colour and its affecting compounds has always been undesirable for both industrial and domestic purpose. More than 8000 types of chemical dye are used in the earth. Dyes are the visible pollutant which mainly pollutes the aquatic life. Every year nearly1 to 2 million kg of dye which are active entering into tour biosphere which may be either in suspended water or dissolved.

The abatement of dye is a major obstacle in field of waste water treatment. This is because dye treatment very important, egenerally those which contains an azo group, are highly stable and more resistant to heat, light and oxidizing agents. As result, they are difficult to remove by most of the conventional methods of oxidizing or biodegradizing process. Other procedures, for instance coagulation and flocculation, photo-degradation membrane-filtration processes (Nano-filtration, electro-dialysis, and reverse osmosis etc.) Nevertheless, its use is limited due to its high cost and because complete color removal has rarely been achieved with it.

There are many conventional method for the treatment with dye effluent such as flocculation (Pans wed& Wongchaisuwan, 1986), reverse osmosis (Cohen, 1978) and activated carbon adsorption (Venkata Rao & Sastry, 1987).These technologies do not reveal significant effectiveness. Low cost methods of treatment have been therefore investigated over a long time. wide range of material for adsorbent preparations .Generally adsorbent's raw material are classified into three categories as (a) Natural material, (b) Agricultural waste/by products, (c) Industrial wastes/ by product.



For instance

- Wood
- Coal
- Peat
- Chitosan/Chitin
- Clays
- Natural zeolites
- Corals
- Bone

For instance

- Shell, hulls, stones from fruits and nuts
- Sawdust
- Corncob waste
- Sunflower stalks
- Straw
- Grass

For instance

- Fly ash
- Blast furnace slug and sludge
- Bagasse, bagasse pith, bagasse fly ash
- Palm oil ash
- Shale oil ash
- Red Mud
- Spent pot lining

A number of non-conventional, low-cost adsorbents have been tried for dye removal. Especially for removal of Safranin dye many adsorbents or activated carbon were used like sodium montmorillonite clay[1], Animal Bone Meal[2], Natural perlite[3], Mineral-Catalyzed Fenton[4] , FS300[5] are categorized as a natural type of adsorbent. In the category of preparation of adsorbent or activated carbon from industrial waste for Safranin dye removal were Waste slurry[6], Red Mud[7], Oil Palm Empty Fruits Bunch[8], Scrap Tires[9], Waste fruit residues[10], Jack fruit peel[11], Banana and Orange Peels[12], Mustard Cake[13] .

Again another category of adsorbent for the removal of Safranin, were used as agricultural waste or by byproduct. Thespusia populinia bark[14], Eichornia Crassipes[15], Almond shell[16], Aalm shell[17], Mango leaf powder[18], Rhizo pusoryzae[19], Photo Catalyst Anatase Titanium Dioxide[20], Cocoa(Theobroma cacao) Shell[21], Cynodon dactylon[22], Azadirachta indica bark[23], Orange peel[24], Jute stick powder[25], Phoenix Sylvestric leaves[26], Wood apple outer shell[27].

1.1 ACTIVATED CARBON

Activated carbon is a pours form of carbon which is manufactures from various carbonaceous raw materials like pine, wood, Coal, Coconut shell, peat, Saw dust, Eucalyptus, Lignite ,Rice husk, etc. It is prepared through carbonization and activation of organic substance. During carbonization most of the non-carbon elements like hydrogen, oxygen are first removed in gaseous form and it develops the internal pores and then after it is activated through chemical activation or stream activation. In activation process, it increases the numbers and dimensions of pores and hence it has large internal surface area. Due to well-developed pore structure and huge internal surface area, activated carbon has an excellent adsorbent capacity in both form powder activated carbon and granular activated carbon.

1.1.1 Application of activated carbon

There is a huge application of activated carbon due to its vast application and lost effectiveness and simple way of use. Following are the usual main use of activated carbon:

- For reducing BOD/COD/Colour from Industrial waste water in the effluent treatment plant.
- For purification of & Gas mask, drinking waterAir.
- For absorbion of moisture from compressed Air for paint shop.
- For De-chlorination of swimming pools & soft drink plant process water .
- For removal of oil from hot condensate etc.

1.1.2 USE OF ACTIVATED CARBON INDUSTRIES

Activated carbon finds extensive use as a purifier colour adsorbed and deodorizer in these following industries, such as:

- In textile Imdustries.
- In dye Intermediates
- In Active Pharmaceutical Ingredients.
- In Pharmaceutical Formulations.
- In food coloring and dyeing industries.
- Organic and Inorganic Chemicals etc.

1.2 OBJECTIVE OF THE PROJECT WORK

The specific objective of these studies to do proper investigation for adsorptive abatement of basic dye Safranin from waste water using self-prepared activated carbon.

i) Preparation of low cost adsorbents with high surface area from biomass/agricultural waste.

ii) Study of different types adsorption and different parameter of adsorption of basic Safranin dye.

iii) Comparative study of Safranin dye removal by new literature with existing literature.

iv) Characterization of all the adsorbents for their various adsorbable properties such as surface area, proximate , TGA,CHNS, FTIR ,SEM, and XRD etc.

v) Kinetic, Equilibrium, Adsorption Isotherms and thermodynamics based on conventional method.

CHAPTER
LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 PRINCIPLE OF ADSORPTION

2.1.1 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. In other words, adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface. It is a surface phenomenon and a consequence of surface energy. The atoms on the surface of the adsorbent are not wholely surrounded by the other atoms and thus, can attract adsorbate.

Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. As the pores are generally small, the internal surface area is greater than the external area. Separation occurs because differences in molecular weight, shape or polarity cause some molecules to be held more strongly on the surface than others. In many cases, the adsorbate is held strongly enough to allow complete removal of that component from the fluid, McCabe smith [29].

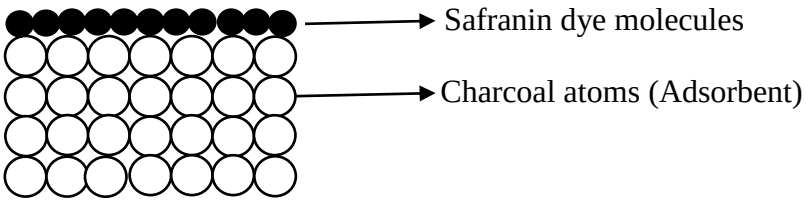


Figure 2.1 Schematic representation of adsorption of dye molecules over the surface of activated carbon

2.1.2 Adsorbate

The fluid which is accumulated on the surface of a liquid or solid is called as adsorbate.

2.1.3 Adsorbent

The solid or liquid on whose surface, the molecules of other substance are adsorbed. Solids, mainly in finely divided state, have large surface area and therefore act as good adsorbents. e.g. activated charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc.

2.1.4 Energy of adsorption

The surface atoms or molecules of adsorbent are relatively unstable due to positive surface free energy. Adsorption is an exothermic process (i.e., ΔH = -ve) i.e., heat is liberated since new bonds are formed. However entropy of the system is also decreased (i.e., ΔS_{sys} = -ve) due to decrease in the number of microstates and decrease in the freedom of movement of molecules. Hence adsorption is thermodynamically more favorable at low temperatures.

The value of ΔG becomes negative, only at low temperatures, when both ΔH and ΔS_{sys} are negative. Therefore, in general, at higher temperatures, the bonds between adsorbate and adsorbent are weakened and the reverse of adsorption i.e. desorption is favored.

2.1.5 Type of adsorption

Depending on the type of attractions between adsorbate and adsorbent and the exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as follows:

(1) Physisorption : In case of physisorption/physical adsorption, molecules are attracted by weak van der Waals forces towards the adsorbent molecules.

(2) Chemisorption: It is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond.

2.1.6 NATURE OF ADSORPTION

Physical adsorption generally is mainly caused by van der Waals force and electrostatic force between the adsorbate molecules and the atoms which compose the adsorbent surface. Thus adsorbents are characterized first by surface properties such as surface area and polarity.

Also some adsorbents have larger pores in addition to micro pores which result from

granulation of fine powders or fine crystals into pellets or originate in the texture of raw materials. These pores called macrospores are several micrometers in size. Macro pores function as paths of diffusion of adsorbate molecules from the outside of granule to the micropores in the form of fine powders and crystals. Adsorbents containing macro pores and micro pores are often said to have "bi dispersed" Pore structures."

2.2 Review on Saranin O dye removal

This review is based on adsorptive mode of Safranin dye removal from wastewater using activated carbons. Many scientist and researcher did many works for the removal of dye. A briefer view of work by the different researcher is presented. All researcher in the followed papers studied the physicochemical parameters such as solution pH, dye concentration, contact time and and have been varied to study the adsorption phenomenon.

1. **Shariati et al., (2011),** investigation was the evaluation of the efficiency of safranin O dye removal with application of magnetite nanoparticles (Fe_3O_4 NPs) as adsorbent. The surface of Fe_3O_4 NPs was modified with addition of sodium dodecyl sulfate as an anionic surfactant. The studies of sorption kinetics of the dye showed a rapid sorption dynamics by a second-order kinetic model, suggesting chemisorption mechanism. Dye adsorption equilibrium data were fitted well to the Langmuir isotherm and the maximum monolayer capacity q_{max} was calculated from the Langmuir as 769.23 mg g^{-1}.
2. **Kumar et al., (2007),** Compared analysis of linear least-square method and non-linear method for estimating the isotherm parameters. Comparison analysis was made using the experimental equilibrium data of Safranin onto rice husk at a solution temperature of 305 K. Sorption data were fitted to Freundlich, Langmuir and Redlich–Peterson isotherm equations. All the three isotherm equations showed a better fit to the experimental data. The results show that non-linear method could be a better way to obtain the isotherm parameters.

   Redlich–Peterson isotherm is a special case of Langmuir isotherm when the Redlich–Peterson isotherm constant *g* was unity.
3. **Namasivayam et al., (1991),** had studied the basic dye removal by biogas waste slurry from aqueous solution. Here rate controlling step is mainly intra particle diffusion. Adsorption rate constant was found to be 0.029 min^{-1} at 20 mg/l initial dye concentration. They found that the adsorption is following Freundlich isotherm. In the pH range 2.3 to 11.2, dye removal was found at least 90%. Desorption of dye in 50% (v/v) acetic acid to

the extent of 69.7% indicate the most dye is held by the chemisorption.

4. **Namasivayam et al., (1996),** had examined sorption onto the adsorbent prepared from waste orange peel. The adsorption obeyed both Langmuir and Freundlich isotherms and the process was following first order rate kinetic. Adsorption capacity was 3.2 mg/g and Acidity pH (=3.0) was favorable for adsorption Safranin dye. Desorption studies showed that alkaline pH was efficient for desorption of RB dye.
5. **Inbaraj and Sulochana (2005)**, they took the jackfruit peel as agricultural waste, for the removal study of the basic dye, from aqueous solution. Among the isotherm models applied to the equilibrium data Redlich-Peterson model better predicted the experimental values. The adsorption capacity was 121.47 $mg.g^{-1}$at an initial pH of 6.0 and at 32 ± 0.5°C. Adsorption capacity increased with increase in temperature. The influence of pH on dye removal was not significant. An optimum carbon dose of 1.2 g/L was required for the maximum removal (96%) of dye from its 60 mg/L solution. A significant portion of the dye was recovered from the spent carbon using 50% acetic acid.
6. **Das et al. (2006),** studies on the removal of a carcinogenic dye Safranin (C. I. 45170) from wastewater by biomass of different mould sand yeasts is described. Among all of the fungal species tested, the biomass of *Rhizo pusoryzae* MTCC 262 is found to be the most effective. Dye adsorption reaches maximum with the biomass harvested from the early stationary phase of growth. The optimum temperature and pH for adsorption are observed to be 40 °C and 7.0, respectively. The adsorption rate is very fast initially and attains equilibrium after 5 h. The adsorption isotherm follows the Langmuir isotherm model satisfactorily within the studied dye concentration range. Of the different metabolic inhibitors tested,2,4-ditrophenol (DNP) and N,N¢-di-cyclo hexyl carbodiimide (DCCD) decrease dye adsorption by ~ 30% suggesting the role of energy metabolism in the process. Spectrophotometric study indicates that the removal of Safranin by *R. oryzae* biomass involves an adsorption process. Scanning (SEM) and transmission (TEM) electron microscopic investigations have been carried out to understand the probable mechanism of the dye-biomass interaction.
7. **Hameed et al., (2007)** had investigated the acidic dye removal by using activated carbon from Rubber (Hevea brasiliensis) seed coat was used. The equilibrium adsorption data of on activated carbon were analyzed by the Langmuir, Freundlich and Temkin isotherm models. The isotherm data were well described by the Freundlich isotherm model. The monolayer adsorption capacity was 227.27mg/g at 30^0 C. Pseudo-first-order; pseudo-second-order and intra particle diffusion models were used to analyze the kinetic data

obtained at different concentrations. The adsorption kinetics was well described by the pseudo-second-order kinetic model. Rubber seed coat-based activated carbon was shown to be a promising material for adsorption of from aqueous solutions.

8. **Arivoli and Thenkuzhali, (2008),** took *Phoenix Sylvestric* leaves as adsorbent, an indigenous agricultural waste was Sulphuric acid treatment was tested for its efficiency in removing. The adsorption followed first order reaction equation and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity, Q_m obtained from the Langmuir isotherm plots were 51.546, 47.236, 44.072 and 41.841 mg/g respectively at an initial pH of 7.0 at 30, 40, 50 and 60 ^{0}C. The temperature variation study showed that the adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the solutions. Almost 90% removal of was observed at 60 ^{0}C. The Langmuir and Freundlich isotherms obtained, positive ΔH^0 value, pH dependent results and desorption of dye in mineral acid suggest that the adsorption of on PSC involves physic sorption mechanism.
9. **Hema and Arivoli, (2009)** were studied on effective removal of using acid treated carbonaceous Thespusia populinia bark adsorbent. Freundlich and Langmuir isotherm plots were 60.836, 64.239, 68.695 and 77.178 mg/g respectively at an initial pH of 7.0 at 30^0,40^0, 50^0 and 60^0 C. The temperature variation study showed that the RB adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significance effect on adsorption was observed on the varying the pH of the RB solution .Almost 79% removal of was observed at 60^0 C .The Langmuir and freundlich isotherms obtained, positive ΔH^0 value, pH dependent results and desorption of dye in the mineral acid suggest that the adsorption of RB on adsorbent involve physisorption mechanism.
10. **Panda et al., (2009),** took Jute stick powder (JSP) as promising material for adsorptive removal of Safranin dye from aqueous solutions. Favorable adsorption occurs at around pH 7.0 whereas temperature has no significant effect on adsorption of both the dyes. The maximum adsorption capacity has been calculated to be 87.7 mg/g of the biomass for .The adsorption process is in conformity with Freundlich and Langmuir isotherms for .Adsorption occurs very fast initially and attains equilibrium within 60 min. Kinetic results suggest the intra-particle diffusion of dyes as rate limiting step.
11. **Xu H Y et al. (2009)**, has studies on natural iron-bearing minerals, schorl could be taken as an effective iron source for degradation of organic pollutants by mineral-catalyzed Fenton-like system. In our present study, the schorl-catalyzed Fenton-like system has been successfully developed for discoloration of an active commercial dye, Safranin, in

an aqueous solution. Through a number of batch discoloration experiments under various conditions, it was found that the reactivity of the system increased by, respectively, increasing schorl dosage, temperature, hydrogen peroxide starting concentration and by decreasing the pH. Over 90% of discoloration ratio could be gained in less than 30 min, and nearly 70% of total organic carbon (TOC) could be removed in less than 200 min. And, the schorl catalyst could be repeatedly used at least ten times, still with high catalytic activity. Comparative studies indicated that the Safranin discoloration ratios were much higher in presence of schorl and H_2O_2 than those in presence of schorl or H_2O_2 only, which suggested that the schorl-catalyzed Fenton-like reaction governed the Safranin discoloration process. The content of Fe ion leaching in the solution was also measured using inductively coupling plasma-atomic emission spectra (ICP-AES). A mechanism proposed herein suggested that adsorption and Fenton-like reaction (heterogeneous and homogeneous) were responsible for the discoloration of Safranin.

12. **Sivaraj et. al. (2010),** studied on the ability of the activated carbon prepared from *Eichornia Crassipes*to remove Reactive Magenta B and Reactive Turquoise Blue dyes from aqueous solution has been carried out as a function of contact time, dose (0.1-0.60 mg/50ml for Magenta B and 0.25-2.0 mg/50ml for Turquoise Blue), pH (2-10) and concentration (25, 50, 75, 100mg.L-1). An amount of 0.6 g of the adsorbent could remove 56.0% of the dye from 100mg.L^{-1}.Magenta B dye solution and 2.0 g could remove .87% of Turquoise Blue dye from 100 mg.L^{-1}.Turquoise Blue dye solution. The amount of dye adsorbed per unit weight of the adsorbent increased from 15.64 to 56.01 mg.g^{-1} with increasing concentration from 25 to 100 mg.L^{-1}. The kinetics of adsorption was 45discussed in view of the kinetic models, the pseudo-first-order Lagergren model, Langmuir, Freundlich, Tempkin, Harkin's-Jura, Elovich and the pseudo-second-order model.
13. **Mohammadi et al. (2010),** did research on Palm shell derived activated carbon was utilized as a potential adsorbent to remove Safranin dye from aqueous solution. Activated carbon was prepared from palm shell through a physiochemical activation process to yield a sample with a Brunauer-Emmett-Teller (BET) surface area of 476.8 $m^2.g^{-1}$. The ability of the prepared activated carbon for dye adsorption was examined in a series of batch experiments. The effect of various process parameters such as initial dye concentration (41.8 to 208.8) μ mol $\cdot L^{-1}$, solution pH (3 to11), and temperature [(30 to 50) °C] on the adsorption capacity of the adsorbent was investigated. Various adsorption isotherms (Langmuir, Freundlich, and Temkin) were used to interpret the experimental data. The obtained sorption data were reasonably described by the Langmuir model. The

Temkin isotherm confirmed the presence of a repulsive lateral interaction in the adsorbent surface. Pseudo first- and second-order kinetic models were used to predict the kinetics of the adsorption process. The obtained results revealed that the adsorption of RB on activated carbon followed a pseudo second-order kinetic model. A maximum dye removal efficiency of 95 % was achieved at an initial dye concentration of 62.6 μmol·L^{-1}, pH = 3, and temperature of 50 °C.

14. **Li et al., (2010),** Activated carbon derived from solid hazardous waste scrap tires was evaluated as a potential adsorbent for cationic dye removal. The adsorption process with respect to operating parameters was investigated to evaluate the adsorption characteristics of the activated pyrolytic tire char (APTC) for Safranin. Systematic research including equilibrium, kinetics and thermodynamic studies was performed. The results showed that APTC was a potential adsorbent for Safranin with a higher adsorption capacity than most adsorbents. Solution pH and temperature exert significant influence while ionic strength showed little effect on the adsorption process. The adsorption equilibrium data obey Langmuir isotherm and the kinetic data were well described by the pseudo second-order kinetic model. The adsorption process followed intra-particle diffusion model with more than one process affecting the adsorption process.
15. **Theivarasu et al., (2010),** removes the Rhodamine-B (RB) from aqueous solutions by cocoa *(Theobroma cacao)* shell activated carbon (CSAC) was studied in a batch adsorption system. The adsorption studies include both equilibrium adsorption isotherms and kinetics. The adsorption equilibrium was represented with Langmuir, Freundlich, Tempkin, Harkin's - Jura and Dubinin-Radushkevich isotherm models. Pseudo first order, pseudo second order, Elovich and Intraparticle diffusion kinetic models were used to test the adsorption kinetics. The kinetic data were well described by the pseudo second order kinetic model. The mechanism of the adsorption process was determined from the intraparticle diffusion model. The results indicated that CSAC could be employed as a low cost alternative for the removal of RB from diluted industrial effluents.
16. **Gupta et al., (2010),** studied on removal of sorption from wastewater effluent. Therefore Mustard cake, obtained from local oil mills, has been characterized and used as an inexpensive and effective adsorbent. The influence of various factors on the adsorption capacity has been studied by batch experiments. The optimum contact time to reach equilibrium was found to be 6 h. Maximum decolorization took place at pH 2.30. The optimum adsorbent dose was 5 g.L^{-1} of particle size < 106 μm. The ongoing adsorption validates both the Langmuir and the Freundlich adsorption isotherms at temperatures of

(40, 50, and 60) °C. Thermodynamic parameters indicate the feasibility of the process. The desorption profile revealed that a significant portion (80 %) of RB dye could be desorbed by using 50 % ethanol as eluting agent. Desorption studies indicated the possibility of recycling and regeneration of both the adsorbent and the dye

17. **Ahamed et al.,(2011),** took carbonaceous adsorbent which were prepared from an agricultural waste, Azadirachta indica bark (AIC), by acid treatment was tested for its efficiency in removing Safranin dye. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity, Q_e obtained from the Langmuir isotherm plots with temperature variation study showed that the RB adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the Safranin solutions. Almost 94% removal of Safranin was observed at 50 °C. Thermodynamic parameters such as ΔH°, ΔS°, and ΔG ° were evaluated. The positive ΔH° value, pH dependent results and desorption of dye in mineral acid suggest that the adsorption of on AIC involves physisorption mechanism.
18. **Parimaladevi and Venkateswaran, (2011),** studies on adsorbent prepare from fruit waste digested with phosphorous (V) oxy chloride (PFR) for Safranin removal. Behavior of adsorption followed pseudo second order kinetics and the rate is mainly controlled by intra particle diffusion. Langmuir and Freundlich models were applied to the equilibrium data. The adsorption capacity (Q_e) obtained from the Langmuir isotherm plots at 302K were 34.48 mg/g and 35.71 mg/g respectively at pH of 7.1 and 6.2. The temperature variation study showed that the adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. By varying the pH of the dye solution significance effect on adsorption was observed. Langmuir and Freundlich isotherms obtained, positive ΔH° value, pH dependent results and poor desorption of indicated that adsorption of these dyes on PFR involved chemisorption mechanism.
19. **Haddad et al, (2012),** studied the adsorptive removal of a cationic dye, Safranin from aqueous solutions was achieved by the use of Animal Bone Meal as a new low cost adsorbent. Adsorption of Safranin Dye was occurred by studying the effects of contact time, adsorbent amount, dye concentration and temperature. Dye adsorption equilibrium was rapidly attained after 60 minutes of contact time. The isotherms of adsorption data were analyzed by the Langmuir and Freundlich adsorption isotherm models. The adsorption capacity (Q_m) obtained from Langmuir isotherm plots were 62.11, 63.69, 64.13 and 64.95 mg/g respectively at 303, 313, 323 and 333°K. Thermodynamic

parameters such as H^0, S^0 and G^0 were calculated, which indicated that the adsorption was spontaneous and endothermic nature. The characteristic results and dimensionless separation factors R_L showed that animal bone meal can be employed as an alternative to commercial adsorbents in the removal of Safranin dye from aqueous solution and wastewater.

20. **Kumar et al. (2012),** In this paper, they studied the feasibility of removal of basic dye Safranin from aqueous solutions by using a low cost natural adsorbent perlite. Batch adsorption experiments were carried out as a function of pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature. Dye adsorption equilibrium was rapidly attained after 50 minutes of the contact time, and it was described by the Langmuir and Freundlich adsorption isotherms over the entire concentration ranges from 20-100 $mg.L^{-1}$. Adsorption data's are used for modeling, from the first and second order kinetic equation and intra-particle diffusion models. Thermodynamic parameters such as ΔH^0, ΔS^0, and ΔG^0 were calculated, which indicated that the adsorption was spontaneous and exothermic nature, which was evident by decreasing the randomness of the dye at the solid and liquid interface. Adsorbent used in this study, characterized by FTIR and SEM before and after the adsorption of Safranin. The characteristic results and dimensionless separation factors (R_L) showed that perlite can be employed as an alternative to commercial adsorbents in the removal of Safranin from aqueous solution and wastewater.

21. **Aliabadi et al. (2012),** had studied the adsorption using almond shell (*Prunusdulcis*) biosorbent has been investigated to remove the Safranin from aqueous solutions. Almond shell has been selected as an adsorbent because of advantages such as high adsorption capacity, nontoxicity, availability and low cost. The effects of contact time, initial dye concentration, adsorbent dosage, particle size and solution pH were studied. The results showed that the removal efficiency increased by increasing contact time, adsorbent dosage and initial dye concentration. In addition, the adsorption was dependent to solution pH and the maximum adsorption was observed at a solution pH of 2.0. The Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption equilibrium data. Freundlich equation fits the experimental data better than the Langmuir and Timken equations do.

22. **Venkatraman et al. (2012),** Here Safranin adsorption from an aqueous solution onto acid activated Cynodon dactylic carbon has been studied experimentally using batch adsorption method. Adsorption Kinetics and equilibrium were investigated as a function of initial dye concentration, pH, contact time, and adsorbent dosage. Kinetic studies

indicated that the adsorption followed reversible First order reaction. Equilibrium data was analyzed using Langmuir and Freundlich isotherm models. The adsorption capacity of Cynodon dactylon was found to be 94 % on the basis of experimental results and the model parameters, it can be inferred that the carbonaceous Cynodon dactylon is effective for the removal of Safranin from aqueous solution.

CHAPTER 3

MATERIAL AND METHOD

3. MATERIAL AND METHOD

3.1 MATERIALS

All the necessary reagents used throughout the project were A.R. grade and procured from Rankem chemicals and Merck chemicals. For the filtration purpose Whatman filter paper of size 40μm, syringe and micro filtrate syringe filter of Whatman 0.45μm were used. The Adsorbents selected for the adsorption studies of Safranin dye procured from Merck chemicals. Stoke Solution of the dye prepared by weighing out the pure powder form solids dye. The agricultural waste biomass was collected from locality of Rourkela.

3.2 INSTRUMENTS

Throughout the project number of instruments were used, which were made the analysis quicker and easier. The supernatant concentration of dye solution was determined by using previously prepared calibration curve at characteristics wavelength λ_{max} = 519 nm, using UV-Visible spectrophotometer which was combined with a computer (*JASCO, V-530, Samsung system*).

Table 3.1 Details of instrument used during research work

Instrument Name	Company Name/Model No.
UV-Visible Spectroscopy	JASCO, V-530
pH meter	SYSTRONICS , μ pH System 360
Shaker	REMI ELEKTRONIK LTD.
Weight Machine	Denver Instrument ,SI-234
BET analysis	Quantachrome Autosorb Automated Gas Sorption System
Ultimate analysis	Vario EL Cube CHNS Analyzer, Elementar CHNSO
SEM	JEOL
FTIR	SHIMANDZU IR PRESTIGE-21

"REMI's hot water bath shaker was used for shaking purpose up to 6 hours for hightemperature and it has 12 holders for holding the 100 ml conical flask size glassware .Hot air oven used for each time for drying purpose. Sieve analysis was done with the help of BSS (British Standard Scale) types of sieves with mesh size Numbers were 16, 18, 20, 25, 30, and 35. Among all mesh sizes maximum quantity of powdered achieved in 30 mesh size (500μm) and selected as regular adsorbent particle size throughout the whole experiments.

3.3 ADSORPTION DEPENDS UPON SEVERAL FACTORS

There are several factors on which the effectiveness of adsorption process depends upon these adsorption conditions which may either be the nature of the adsorbent (acidic/ basic) or the characteristics of adsorbent which includes the high surface area, pore size distribution, ash content and hydrophobicity.

The acidity or basicity of the activated carbon depend upon the presence of hetero atom's such as oxygen, which can form phenols, ethers, lactones ketone, carboxyl and nitrogen in the form of amines and nitro groups; and phosphorus as a phosphate can be determined.

On the other hand, adsorption also depends on the nature of the adsorbate depends on its hydrophobicity, polarity, and size of the molecule.

In search of alternative of commercial Activated carbon, low cost adsorbent are investigated. Broadly, the raw materials used for the preparation of novel adsorbents are classified under three main categories: Agricultural Waste (AW) Industrial Waste (IW) Mineral Waste (MW).

3.4 ADSORBENT PROPERTIES

The activated carbon prepared from biomass, used for adsorption process. Here four different materials are used for preparation of adsorbent and their characterizations are done.

3.4.1 Physico-chemial properties of adsorbent

Density, Porosity, Specific gravity, bulk density and dry density were determined with the help of specific gravity bottle of 50 ml capacity using following equations

$$Sp.gravity = \frac{(W_2 - W_1)}{[(W_4 - W_{1)} - (W_3 - W_2)} \qquad (3.1)$$

Where,

W_1 = Wt. of the empty density bottle

W_2 = Wt. of the (1 gm of the sample+ density bottle)

W_3 = Wt. of the (water+1 gm of the sample+ density bottle)

W_4 = Wt. of the (water++)

W_5 = Wt. of the sample

Void Fraction (e) and porosity of adsorbents were calculated by using Equations:

$$porosity = \frac{e}{1+e} \qquad (3.2)$$

Table 3.2 Physio-chemical properties if adsorbent

Properties	Activated Blackberry Carbon
Specific gravity	0.969
Bulk density, g/ml	3.466
Dry density	1.293
Void ratio	0.289
Porosity	0.433

3.4.2 pH

The pH of bio-char was determined according to Novak et al. [36] and Cheng and Lehmann [33]. Two grams of bio-char were shaken (REMI) with 40 mL distilled water or 1 M KCl (99% of purity Merck Chemicals Ltd.) solution for 30 min. This suspension was allowed to stand for 10 min before measuring the pH with a pH electrode.

The pH of char sample was determined in both water and KCl solutions. For the measurement pH in water, 40 ml of water taken in conical flask and adsorbent of 1gm in added to in the solution of water and kept the dispersed solution in shaker for 1 hours for

proper mixing. Initial pH and final pH was measured, after addition of adsorbent change in pH, is due to surface chemical property. Similarly with 0.1 M KCl, pH was measured .In 40 ml of 0.1 M KCl, 1gm of adsorbent putted and kept in shaker for 1 hours.

Table 3.3 pH measurement results:

Name of sample	Initial pH (with water)	Final pH (with Water)	Initial pH (with KCl)	Final pH (with KCl)
Blackberry seed	6.11	6.43	6.42	5.83

3.4.3 BOEHM TITRATION

Surface acidity and alkalinity using Boehm titration method Boehm titration provides an indication of the total surface acidity and alkalinity of the bio char, and is based on the method described by Cheng and Lehmann [34]. A 0.15 g subsample of bio-char was added to 15 mL of either 0.1 M NaOH or 0.1 M HCl solutions (Merck Chemicals Ltd.) and shaken with an end-over-end shaker for 30 h. The bio-char slurry was then filtered using a Whatman no. 40 filter paper. An aliquot of 5 mL of the NaOH filtrate was transferred to a 10 mL 0.1 M HCl solution that neutralized the unreacted base. The solution was back-titrated with 0.1 M NaOH with a phenolphthalein indicator. Surface basicity was measured similarly to the measurement of surface acidity and an aliquot of 5 mL of the HCl filtrate was directly titrated with 0.1 M NaOH. The base or acid uptake of BC was converted into the content of surface acidity or surface basicity (m.mol g^{-1}), respectively.

3.5 RAW MATERIAL FOR ADSORBENT PREPARATION

We took Blackberry seeds biomass for preparing activated carbon by following common method of activation, chemical method. Activated carbon, prepared from this biomass is depended upon the nature of construction and chemical formation [6, 8, 10, 11, 41, and 42].

(I) Syzygium cumini (Blackberry seeds)

Syzygium cumini commonly known as jamun, is an Indian tropical tree found largely in the central and north Indian plains and forests. It is a fast growing tree that grows very alarmingly, possesses evergreen or semi-evergreen foliage, and belongs to the family Myrtaceae.

Table 3.4 Scientific Classifiaction of Syzygium cumini seed

Kingdom		Plantae
Order	:	Myrtales
Family	:	Myrtaceae
Genus	:	Syzygium
Species	:	S. cumini

a. Jamun tree with fruits

b. Raw dried Blackberry Seeds

c. Carbonized Blackberry Seed

d. Activated Blackberry carbon of 500 µm

Figure 3.1 Systematic preparation of Seed to Activated Carbon of Syzygium cumini

3.5.1 Steps of adsorbent Preparation:

Preparation of activated carbon has been done by various methods

First, Raw material (Jamun seed) were washed 2 to 3 times with general pipe water for removal of mud, dust and unwanted external materials

i. Use single distilled water for second time washing purpose, then dried the material up to 75^{o}C to 95^{o}C for 1hr.

ii. The dried material was transferred into the pyrolytic reactor and reactor put inside the furnaces, by maintaining 370^{0}C.

iii. After pre-carbonization of material, material are crushed into powder or granular form using hand blender.

iv. After blending of carbonaceous material, we sized it with the help of sieving technique by taking different size of sieve and choose the 30 BSS (British Standard Scale) sieve which was 500 micron size as our particle size.

v. Resulting sample is washed with distilled water and unwanted material gets separated as waste filtrate.

vi. Properly washed carbonized carbon is impregnated with nitric acid acid solution with an impregnated ratio (W/V) of 1:5 solid/liquid ratio for nearly 20 hours.

vii. Resulting chemically acid washed Activated Carbon was again washed with single distilled water continuously up to a constant pH reached.

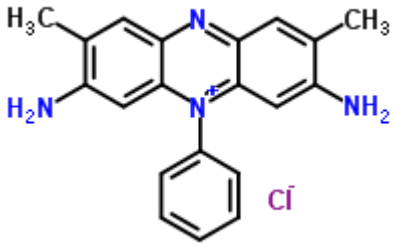
viii. Finally the washed AC is kept in the oven at 110^{o}C for 3hrs for removal of moisture.

ix. Dried activated adsorbent kept in plastic storage bottle container for further use.

3.6 ADSORBATE

3.6.1 Safranin dye

Of the various dyes, basic dyes are the among the brightest class of soluble dyes which is generally used by the textile industry, as their tinctorial value is very high. Safranin(O) is a basic dye which is widely used in textile, trace, biological laboratory purpose. Safranin is a red dye used to dye silk, wool, and tannin mordant cotton.



Safranin

IUPAC Name-: (3, 7- Diamino - 2, 8 – dimethyl - 5-phenylphenazin – 5 – Ium chloride)

Common Names: Safranin (O), Basic Red 2.

In addition to its enormous application in dye industries Safranin is generally used as a biological staining in many biomedical research laboratories and also the dyeing of leather and paper. These biological stains are known to be toxic to human and animals.

3.6.1.1 Physical properties of adsorbate (Safranin dye)

Properties	Safranin dye
Chemical formula	$C_{20}H_{19}ClN_4$
Common Chemical Name	Safranin, Safranin O or Basic Red 2
IUPAC Name	(3,7- Diamino-2,8-dimethyl-5-phenylphenazin-5-ium chloride)
Molecular Mass (g/mole)	350 g/mol
Vapor pressure (mm Hg at 20 0C)	100 k Pa
Nature	Powder
CAS No.	477-73-6

3.8 Preparation of Standard Stock Safranin (dye) Solution

1gm of powder dye was dissolved accurately in 1000ml of distilled water container. First of all, in one liter measuring flask small quantity less than of double distilled water

taken and mixed the weighed 1gm of powder Safranin dye into it. Then the dye solutions had shaken thoroughly. Finally single distilled water was poured up to the one liter mark of measuring flask. The stoke solution prepared was 1000mg.L^{-1} with single distilled water and next lower concentration prepared by subsequent dilution. The supernatant dye solution was analysis with λ_{max}= 519 nm using JEOL UV-Visible Spectrophotometer.

3.8.1 Analytical measurement of Safranin dye

The standard calibration curve of known concentrations of Safranin dye was plotted to find the absorbance at characteristic wavelength of λ_{max} = 519nm. A spectrophotometer (JEOL UV/Vis-530) was used for the calibrating, which shows a linear variation of absorbance up to 30 mg/L concentration. Hence, the samples with higher concentration above 10ppm (mg/L) of dye were being diluted by 5 or 10 times with distilled water.

3.9 ADSORPTION STUDIES

3.9.1 Experimental methodology used for the adsorption

Many researchers investigated by following several methods and techniques to stimulate the contact between adsorbent and adsorbate for the maximum up taking of pollutant from aqueous medium. Initially calibration curve done before adsorption studies to generate the equation, which implies absorbance is the function of concentration.

Broadly, adsorption studies done in batch contact system method or continuous flow system method. Here all the studies of optimized operational variables done in batch contact system method. For all experiments including the adsorption Kinetics, isotherms, thermodynamics, were being determined by batch method which easy and simple to execute.

3.10 BATCH CONTACT SYSTEM ADSORPTION STUDIES

Generally in batch contact process, graphically determined amount of adsorbent was agitated in a specific volume of adsorbate solution having known concentration for a certain period of time until the concentration of adsorbate in solution phase decrease to a desirable level. The removal rate of adsorbate mainly depend upon the force of driving the rate of the adsorption and solution concentration as physical parameters and surface area, porosity .of adsorbent as morphological parameters, acidity or basicity nature of adsorbent also important parameters. Preliminary experimental done to optimize the adsorbent dose and agitation time.

In the present studies, a series of batch adsorption experiments were conducted to determine the adsorption of Safranin on Activated Blackberry seeds (ABC). All the batch adsorption experiments were performed in a mechanical shaker equipped with a thermostatic water bath at constant speed of 120 rpm using 100 ml conical flasks with stopper containing 50 ml each of dye solutions of 100 ppm concentration. Experiments were performed at room temperature of 27 ^{0}C (300 K). The pH of the solution was maintained natural as well as desire done when needed likewise the other parameters such as adsorbent doses, temperature, contact time were also either varied or kept at desired level as per the need. All solution samples post adsorption were filtered through syringe driven Millipore Whatman (0.45μm) filter sockets. The concentrations of dye in treated samples were determined by UV spectrophotometer and by comparing with calibration equation the amount of dye adsorbed per unit mass of the adsorbent was evaluated by using the following equation,

$$Q_t = \frac{(C_0 - C_t)}{m} v \qquad (3.3)$$

The percentage removal of Safranin dye was calculated by the following equation,

$$\%removal = \frac{(C_0 - C_t)}{C_0} * 100 \qquad (3.4)$$

3.11 OPTIMIZATION OF OPERATIONAL VARIABLES

In this section, effect of different parameters or operational variable such as effect of adsorbent dose, Contact time, initial concentration, pH and temperature on the adsorption of Safranin dye by ABC have been examined. Kinetics studies for the removal of the dye under the given condition have also been to understand the mechanistic role of the system. The experiments were repeated twice and suitable resulted value was reported.

3.11.1 EFFECT OF ADSORBENT DOSE

The adsorbent effect (ABC) dose on the Safranin adsorption was investigated by the varying the amount of dose from 0.2g to 3.2g (with 0.2 difference in dose quantity) in 50ml dye solution. These experiments were conducted at natural pH using 25mg/L or 25 ppm of initial dye concentration for exactly 360 minutes. The minimum amount of adsorbent corresponding to the cross section of uptake capacity and percentage removals.

3.11.2 EFFECT OF CONTACT TIME

The contact time effect on the adsorption of Safranin dye on to ABC were studies in the range of 0 to 360 minutes (as 15,30,45,60,120,180,240,300 and 360 minutes). This study was carried out at natural pH of all dye solution using 50 ml of 25 mg/L of initial adsorbate concentration and 1.25 g/L of ABC.As the time of agitation increases, the intimate contact between sorbate-sorbent increased and all the pores of adsorbent was occupied by the adsorbate in monolayer fashion initial stages.

3.11.3 EFFECT OF PH

Effect of pH on the adsorption of Safranin dye by ABC was studies in the pH range 2.0 to 12.0. The pH of Safranin solution was being adjusted before the experiments by using the 0.1M NaOH and 0.1M HCl. The values of pH of the solution were measured prior and after the asorption process and difference in pH was determined. This study was conducted with 50 ml of 25 PPM initial adsorbate concentration and 1.25 g/L of ABC.

3.11.4 EFFECT OF INITIAL CONCENTRATION

The initial adsorbate concentration (C_0) effect on the adsorption by ABC was examined by ranging the initial concentration from 5-25 mg/L of 50 ml. This study conducted at pH 6 with adsorbent dose 1.25 g/L for. Time of agitation for this experiment was 360 minutes.

3.11.5 EFFECT OF TEMPERATURE

Here investigation was done and the influence of temperature on the sorption rates was examined at four different temperatures (25^0C, 35 ^{0}C, 45 ^{0}C and 55 ^{0}C). The Effect of the temperature for the adsorption of Safranin dye was studied at pH 6 for ABC with 1.25g/L adsorbent dosage for 360 minutes with 50 ml dye solution having six different concentration (5, 10, 15, 20, 25 and 30 mg/L). From this temperature effect, different isotherms studies were also did for choosing of better fitting isotherm.

3.12 THERMODYNAMIC PARAMETERS

As adsorption is a kinetic process, its removal rate can be increased or decreased by increase or decrease in the system temperature. The Gibbs free energy change (ΔG^0) of the asorption process is related to the equilibrium constant by the classic Van't Hoff equation

$$\Delta G^0 = -RT \ln k_d \qquad (3.5)$$

From thermodynamics, the Gibbs free energy change is related to the entropy change and heat of adsorption at constant temperature by the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (3.6)$$

$$R \ln k_d = \frac{-\Delta G_0}{T} = \Delta S^0 - \frac{\Delta H^0}{T} \qquad (3.7)$$

Where, K_d is the distribution coefficient, H^0 is the enthalpy change (kJ/mol), is the entropy change (J/K. mol), R is the gas constant (8.314 J/K. mol) and T is the temperature in kelvin.

When the process is endothermic ($\Delta H^0 > 0$), its equilibrium constant increases with increase in temperature, if the process is exothermic ($\Delta H^0 < 0$), the equilibrium constant decreases as temperature is raised. Gibbs free energy of the specific sorption was calculated from the well-known equation (3.9).The thermodynamic parameters ΔH^0 and ΔS^0 were obtained from the slope and intercept of the linear Van't Hoff plot ($R \ln K_{d\,VS.} 1/T$).

3.13 MODELING OF ADSORPTION ISOTHERMS AND ITS STUDIES

In order to determine the efficiency of adsorbent, the equilibrium adsorption of the Safranin dye was studied as a function of concentration .Various equilibrium models have been developed in order to describe sorption isotherm relationships. Any particular may be fit experimental data accurately in one set of conditions, but may be fall entirely under another. No single model has been found to be applicable in generals. The sorption of capacities of Activated Blackberry seed carbon (ABC) for Safranin have been evaluated using different isotherms, namely Langmuir, Freundlich, Temkin and Dubinin-Raushkevich (D-R) isotherms.

3.13.1 Langmuir Isotherm

The most commonly used adsorption isotherm equation used for modeling o the adsorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number identical site and is given by following equation"

$$q_e = \frac{a_l b_l c_e}{1 + b_l c_e} \qquad (3.8)$$

In general, Langmuir theory has the basic assumption i that the sorption takes place at the specific homogeneous sites with in with in the sorbent. The linearized form of Langmuir isotherm are as follows:

$$\frac{c_e}{q_e} = \frac{1}{Q_{\max} b_l} + \frac{c_e}{Q_{\max}} \qquad (3.9)$$

Where,

$Q_{\max}$ = monolayer adsorption capacity, ($mg.g^{-1}$), relates about tthe solid phase concentration,

With respect to the complete coverage of available asorption site, can be evaluated from the slope of Langmuir isotherm plot (C_e/q_e against C_e)

b_l = Constant for Langmuir Isotherm , ($L.g^{-1}$) ,This value corresponds to energy of sorption, calculated from the intercept calculated from the linear plot of Langmuir isotherm.

Iinfluence of the isotherm shape for 'favorable' and 'unfavorable' sorption is on the basis of criterian of feasibility, was studies by Weber and Chakraborti .The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless separation factor ,R_L ,which describe the type of isotherms and is defined by,

$$R_L = \frac{1}{1 + b.c_0} \qquad (3.10)$$

B stands for Langmuir constant which came into existence in equation (3.13) & C_0 term is the initial concentration. Thsese parameters show the shape of the isotherm for the R_L values taking their places between 0 to 1, then favorable adsorption indicated. If the R_L value is

greater than one then the adsorption is considered to be unfavorable , on the other hand if the adsorption value comes as one then the it comes a linear and unfavorable graph and at last if the adsorption value comes as zero then it indicates an irreversible process.

3.10.2 Freundlich Isotherm

The freundlich isotherm model is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface, the freundlich model is non-linear & linear form can be expressed as:

$$q_e = k_f (c_e)^{\frac{1}{n}} \tag{3.11}$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln c_e \tag{3.12}$$

Where, K_F is the freundlich characteristics constants and 1/n the heterogeneity factor of adsorption, obtained from intercept and slope of ln (q_e) vs ln (C_e) linear plot respectively.

The K_F value indicates the adsorption capacity and is also used for measuring the effective surface area . B and 1/n are related to enthalpy and intensity of the adsorption. 1/n value should be less than unity for high adsorption capacity.

3.13.3 Temkin Isotherm

The Temkin equation isotherm assume that the heat of adsorption of all the molecule in the layer decreased linearly with coverage due to sorbent-sorbate interaction and that adsorption is being characterized by uniformity in distribution of the binding energy, up to some extent maximum binding energy . The value of Temkin constant along with the coefficient of determination. The Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b \ln(k_t c_e)} \tag{3.13}$$

Equation 3.17 can be linearized as:

$$q_e = B_1 \ln k_t + B_1 \ln c_e \tag{3.14}$$

Where (B_1=RT/b) and K_T, the equilibrium binding constant (L/mg) which

corresponds to the maximum binding energy and constant B_1 which is related to the heat of asorption. A plot of q_e versus ln (C_e) is useful for the determination of the isotherm constant K_T and B_1.

3.13.4 Dubinin-Radushkevich (D-R) Isotherms

Dubinin-Radushkevich (D-R) isotherm model is used for pore filing nature of the asorption process and its equation can be given as: in Ahmaruzzaman et.al. [29]

$$\ln q_e = \ln X_m - \beta\varepsilon^2 \qquad (3.15)$$

Where q_e used is the amount of adsorbate adsorbed onto the adsorbent and Xm (mg/g) signifies the maximum adsorption capacity of sorbent, β being constant which is related to adsorption energy, while ϵ ibeing Polanyi sorption potential ,which can be calculated by using following equation:

$$\varepsilon = RT \ln(1 + \frac{1}{c_e}) \qquad (3.16)$$

Where R being the gas constant in kJ/mol K, T is temperature in kelvin and Ce is the concentration of adsorbate in equilibrium in solution.

When we plot ln (qe) against ϵ^2, we obtain a straight line. The slope of the plot determines the value of B and the intercept signifies the value of sorption capacity Xm. The constant β provides the mean free energy 'E' of asorption per molecules of sorbate when it is being transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (3.17)$$

The value of E provides information about the sorption mechanism whether it is ion-exchange, chemical or physical adsorption.

3.14 ADSORPTION DYNAMICS

The kinetic of sorption is significant from the point of view that it controls the efficiency of the process. The characterization of adsorbent surface is a crucial factor that affects the parameters rate and that diffusional resistance also plays a vital role in the overall

transport of the solute .The kinetics of sorption that define the efficiency of sorption of Safranin dye were determined by the pseudo first order or pseudo second order models.

3.14.1 Pseudo First Order Model

The first order rate expression given by langergren:

$$\log(q_e - q) = \log q_e - k_{ad}(\frac{t}{2.303}) \qquad (3.18)$$

Where, q_e and q are the amount of dye adsorbed (mg/g) at time t (min) and at equilibrium time, respectively and k_{ad} is the rate constant of the adsorption [30~32, 34, 36, 37].

For controlling of kinetics four steps were present, (a) mass transfer metal ions from boundary film to surface mass transfer of solute from solution to the boundary film (b) mass transfer metal ions from boundary film to surface, (3) sorption and ion exchange of ions onto site, (4) internal diffusion of solute. This step is assumed to be very rapid and non-limiting in this kinetic analysis: sorption is a rapid phenomenon. The first as well as the second steps are external mass transfer resistance steps, which depends on various parameters such as agitation and homogeneity of solution. The fourth one was particle diffusion resistance step.

From the kinetic equations, the forward and backward rate constants, the overall rate constant were calculated at variable parameter concentration and temperature. The adsorption of chromium from liquid to solid phase can be expressed as:

Here forward reaction constant is K_1, and Backward reaction constant K_2.

$$A \underset{k_2}{\overset{k_1}{\longleftrightarrow}} B$$

Where, K_1 being the forward reaction rate constant, k being the backward reaction rate constant. By using the kinetic equations overall rate constant, the forward as well as backward rate constants was calculated at different temperature. By plotting ln $(1-Ut)$ versus t ,the overall rate constant k for given concentration of Safranin was calculated by considering the slope of straight line in Fig. for various temperature and concentration (Rengaraj et al.[30]) .By using equations in reference, , forward and backward rate constants, the equilibrium constant Kc, k_1 and k_2 were calculated and shown in Table . From the table, it is observed that the forward rate constants used for the removal of B dye is greater than the

backward rate constants namely the desorption process. This result reveal that the rate of adsorption is clearly dominant.

3.14.2 Pseudo Second Order Model

The pseudo 2nd order model can be represent in the following form, Ahmaruzzaman et.al. [29].

$$\frac{dQ_t}{dt} = k_2(q_e - q_t)^2 \qquad (3.19)$$

Where, K_2 being the pseudo second order rate constant (g/mg .min). After integrating the equation (3.19) for boundary conditions $q_t=0$ at t=0 and $q_t = q_t$ at t=t, the following equation is obtained

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^{\,2})} + \frac{1}{q_e}.t \qquad (3.20)$$

$$h = k_2 q_e^{\,2} \qquad (3.21)$$

The initial adsorption rate h (mg/g.min), the pseudo second order constant K_s the "equilibrium sorption capacity (qe), can be calculated from the slope and intercept of plot t/q_t vs. t.

CHAPTER 4
RESULT AND DISCUSSION

4. Result and Discussion

In this section, different experiments were done and these experimental results were very nicely discussed on the basic of scientific occurrence.

4.1 Calibration Curve

A calibration is a general method of determining the concentration of a substance in an unknown sample by comparing it with the known concentration having a set of standard sample. It knows as analytic signal as because of the calibration curve plotted according to the instrumental response and it changes with concentration of the measured substance (analyte).The operator prepares a series of standards across a range of concentrations near the expected concentration of analyte in the unknown. The concentrations of the standards must lie within the working range of the instrumentation. For most analyses a plot of instrument response vs. analyte concentration will show a linear relationship. The operator can measure the response of the unknown and, using the calibration curve, can interpolate to find the concentration of analyte or the unknown concentration.

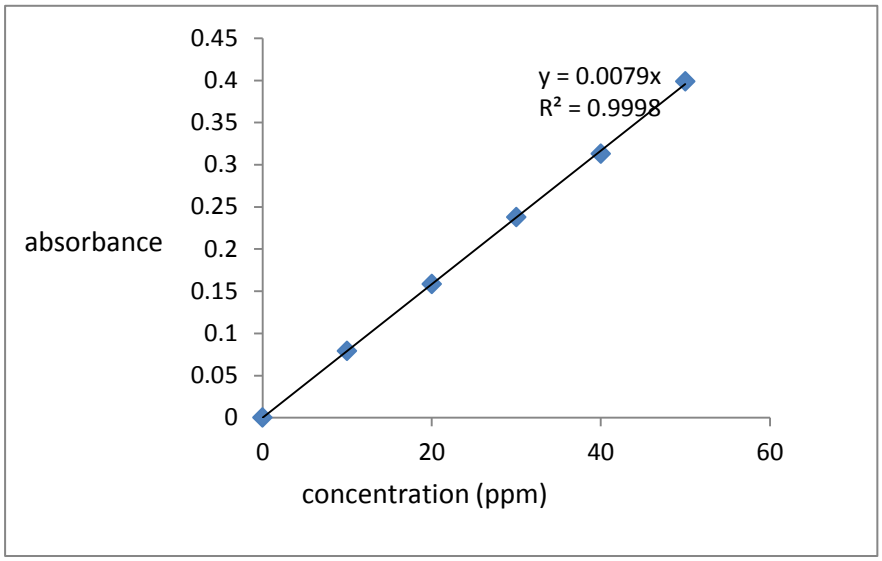


Figure 4.1 Graphical representation of calibrating of unknown Safranin dye concentration in the water sample, C_0 = 0-50 mg/l, T = 25^0C

In the calibration curve method, a series of external standard solutions is prepared and measured. A line or curve is fit to the data and the resulting equation is used to convert readings of the unknown samples into concentration. An advantage of this method is that the

random errors in preparing and reading the standard solutions were averaged over several standards. Moreover, non-linearity in the calibration curve can be detected and avoided (by diluting into the linear range) or compensated (by using non-linear curve fitting methods).

When an unknown sample is measured, the signal from the unknown is converted into concentration using the calibration curve.

Preparation of a series of "standard solutions" of the substance that you intend to measure, measure the signal (e.g. absorbance, if you are doing absorption spectrophotometry), and plot the concentration on the x-axis and the measured signal for each standard on the y-axis. Drawing a straight line as close as possible to the points on the calibration curve (or a smooth curve if a straight line won't fit), so that as many points as possible were right on or close to the curve.

4.2 Various parametric effects on the adsorption of Safranin dye onto Activated Blackberry carbon (ABC**)**

4.2.1 Effect of adsorbent (ABC) Dosage on adsorption

In adsorption studies the adsorbent dose play an important role, because of effective removal of adsorbent and cost of used adsorbent .Using of less adsorbent dose then the required achievable removal or using more costlier adsorbent dose for getting optimum removal, so to answer these drawbacks, choosing of intermediate path is always cost effective path for maximum removal with minimal resources. So there is huge importance for the study of effect of adsorbent doses on adsorption for all adsorption studies [30, 33, and 37].

In order to study the effect of adsorbent dosages, different dosages of ABC (Activated Blackberry seed carbon) were taken as varies from 0.05 g to 0.5 g into series of 100 ml conical flasks which contain 50 ml of Safranin dye of 25 PPM (25 mg/l) concentration. The sample is kept in shaker for 6 hours with nearly 120 rpm for better mixing at solid liquid interface. Here natural pH was maintained. A plot of Qe and % removal was plotted on same axis against the adsorbent dosage.

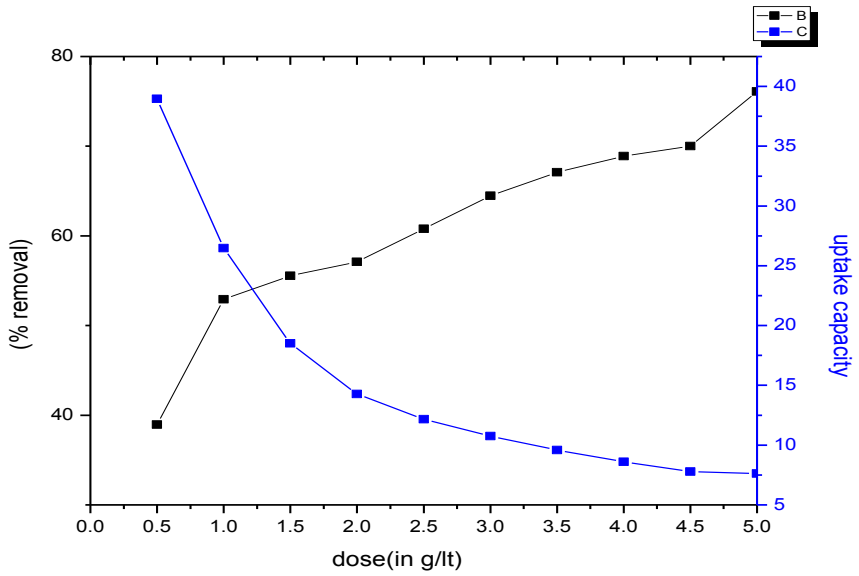


Figure 4.2 Graphical representation of adsorbent dosage on adsorption process

It was found in the Fig.4.2, that with increase in ABC adsorbent dose percentage removal is increased because large amount of adsorption sites were found, in contrast the uptake of Safranin dye is gradually decreased because of two reasons, firstly for the same amount of Safranin dye large number of adsorption sites were found and secondly large amount of adsorbents in the small available space clump together thereby limiting the path of diffusion and thus adsorption. The corresponding point on x-axis of the intersection point of these two curves give the optimal dose of adsorbent and here we found the optimal dose for ABC as 0.0625g/ 50 ml (1.25 g/l) of Safranin dye solution.

4.2.2 Effect of Contact time on Safranin-ABC System.

To investigate the effect of contact time on adsorption of Safranin dye (C_o =25 mg/L), the batch experiments were carried out in a series of conical flasks with a constant AMC dose of 0.0625gm/50 ml in all the samples as optimal dose. These flasks were agitated in water bath shaker for 15, 30, 45, 60, 120,180,240,300 and 360 minutes at a constant 120 rpm at the natural pH in all the samples. The samples were withdrawn from the water bath shaker at predetermined time intervals. The settled supernatants were bring out from flask using pipette after giving sufficient time and subsequently with syringe driven Whatman Millipore filter of pore size 0.45µm.The concentration of dye in supernatant was measured for all the samples. The Qe was evaluated for all the samples and a graph was plotted between Qe vs time.

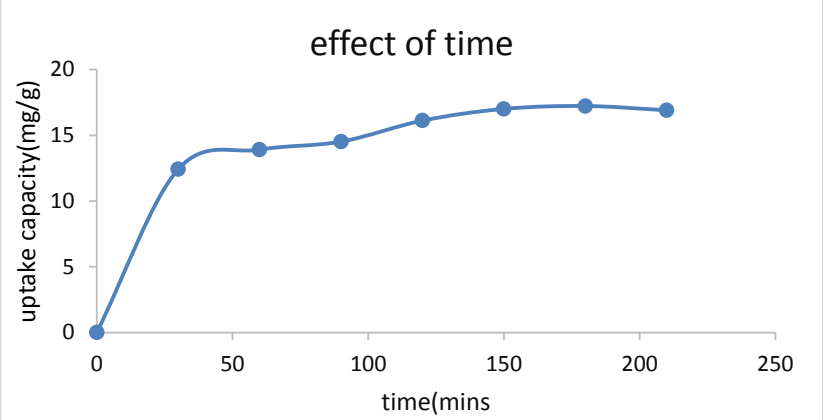


Figure 4.3 Graphical representation of contact time effect on adsorption process

From this above graph, we explained that nearly after 120 minutes Qe equilibrium reached and % Removal also became constant, so the optimal contact time was 120 minutes. This optimal time period was the sufficient time for stabilization of this adsorbent and adsorbate dispersed solution.

4.2.3 Effect of pH on Safranin-ABC system

One of the most important parameters controlling the adsorption process is pH.

The effect of initial pH on the adsorption of dye was also evaluated at 25^0C at different initial pH values in the range of 2–12 for initial concentrations of 25 mg/l for Safranin dye solution adjusted by adding either 0.1M HCl or 0.1M NaOH. The effect of pH of the solution on the adsorption of Safranin on ABC was determined. The pH of the solution was controlled by the addition of 0.1M HCl or 0.1M NaOH. The uptake of Safranin at pH 11.0-12.0 was the minimum and a maximum uptake was obtained at pH 6.0. However, when the pH of the solution was increased (more than pH 2), the uptake of Safranin was increased. It appears that a change in pH of the solution results in the formation of different ionic species, and different carbon surface charge. At pH values lower than 6, the dye can enter into the pore structure. At a pH value higher than 6, the zwitterions form of Safranin in water may increase the aggregation of Safranin to form a bigger molecular form (dimer) and become unable to enter into the pore structure of the carbon surface. Due to the amphoteric character of a carbon surface, its adsorption properties may be influenced by the pH value of the solution.

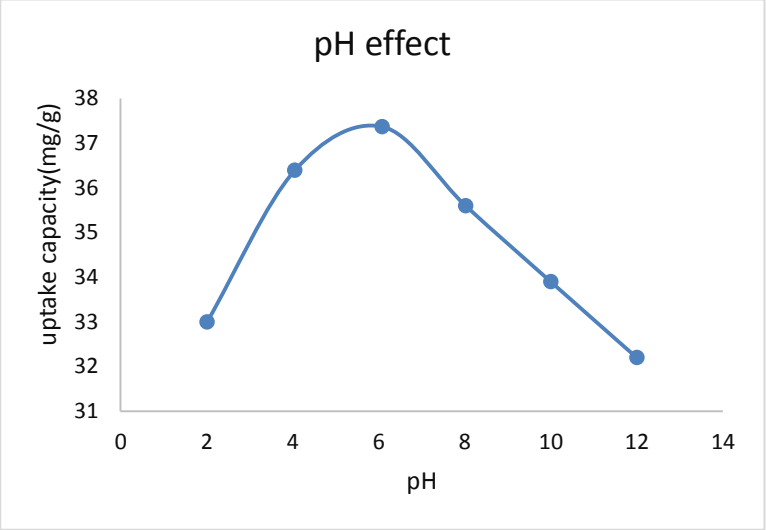


Figure 4.4 Graph of pH effect on adsorption process

4.2.4 Point Zero Charge for Safranin-ABC system

The pH at the potential of zero charge of the carbon (pH_{zpc}) was measured using the pH drift method. pH taken as 1.05,2,3,4,5,6,7,8,9,10,11,12 and 12.93.

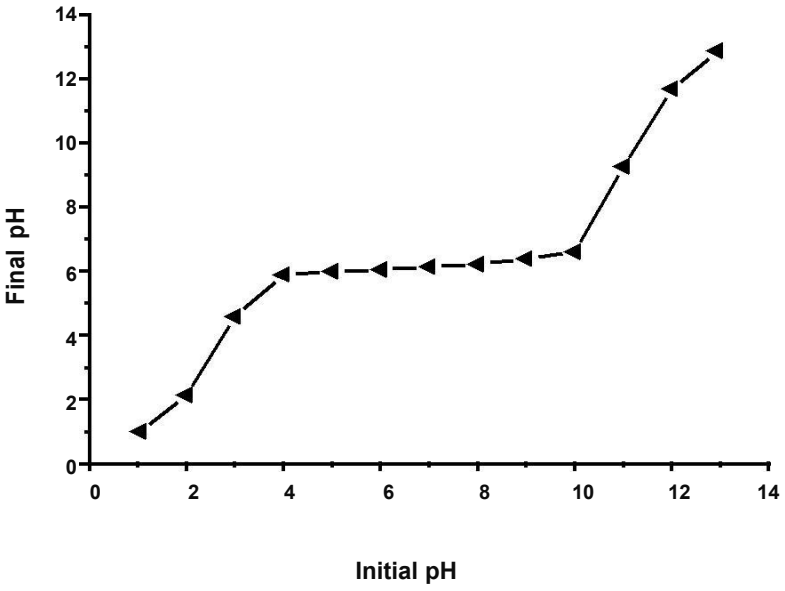


Figure 4.5 Graph of pH final pH vs initial pH for zero point charge study

The pH of the solution was adjusted by using 0.1 M sodium hydroxide or hydrochloric acid. 1 g of the activated carbon was added to 50 ml of 25 ppm solution. After stabilization, the final pH was recorded. The plot of final pH versus initial pH was used to determine the zero point charge of the activated carbon [38, 40].

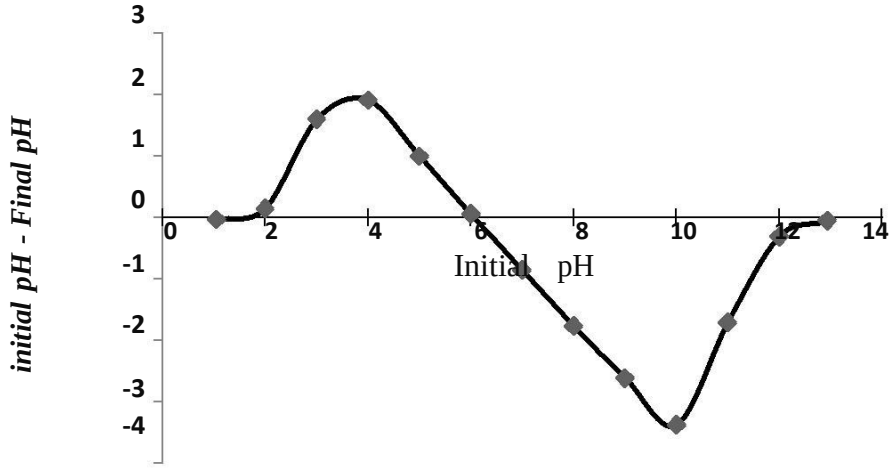


Figure 4.6 1 Graphical representation of initial pH vs change in pH

Therefore, it can be assumed that pH_{zpc} of Safranin dye-AMC system is pH 6.0. Then surface of the activated carbon ABC is negatively charged above the pH_{zpc}, and positively charged below the $pH_{zpc.}$ The magnitude of surface charge of activated carbon decreases with increase in pH. Thus, electronegativity of activated increases with increase in pH. The lower removal of the positively charged dye at acidic pH range is probably due to the presence of excess H^+ ions was competing with the dye molecule for the adsorption site. At alkaline pH, adsorbent surface gets net negative charge.

4.2.5 Effect of initial Concentration of Safranin-ABC system

To study the effect of initial dye concentration, experiments were carried out in different conical flasks with a fixed adsorbent dose of 0.0625g/50ml at varying Safranin dye initial concentrations of 10, 15, 20 and 25 $mg.L^{-1}$.All the solution maintained the pH as 6.0. Each particular dye concentration shaking for 15,30,45,60,120,180 minutes.

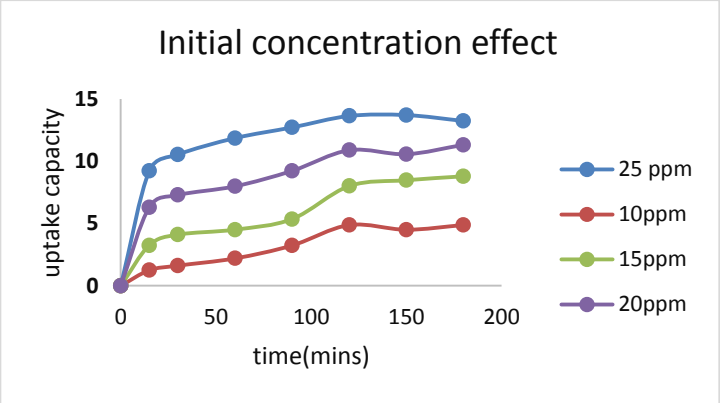


Figure 4.7 Graphical representation of initial concentration effect on adsorption process

The samples were withdrawn from the shaker at the mentioned time intervals. Post adsorption the supernatant was collected and filtered, first using then by syringe driven 0.45µm Millipore whatman filter. Filtered supernatant was analyzed using spectrophotometer and a graph was plotted with Qe versus time. The adsorption data for the uptake of phenol versus contact time at different initial concentrations is represented in Fig.4.7.

From the Fig.4.7, here the pattern of graph showing that with the increase in contact time between Safranin-ABC system, the uptake capacity increases unto 120 mins and then equilibrium is reached also the uptake capacity increases with the increase in the Safranin concentration due to the availability of more number of adsorbate. Hence the highest concentration 25 ppm of adsorbate is taken as an optimum Safranin concentration for further studies. The higher uptake capacity with the increase in adsorbate concentration may be attributed with the higher concentration gradient for the same amount of adsorbent dose.

4.2.6 KINETICS OF ADSORPTION

Generally for kinetics of adsorption study pseudo-first-order and pseudo-second order models were considered. The different results were collected from these graphs. The contact time study can be used to determine the rate limiting step in the adsorption process with the help of a Weber –Morris plot. The possible rate limiting steps were mass transfer from the bulk liquid phase to the particle external surface, film diffusion and inter particle diffusion.

Kinetic of adsorption of ABC and Safranin dye system

The time dependent batch adsorption data using fixed dose 0.0625 gm/50 ml with pH = 6 maintained of adsorbent at 25 ^{0}C was used for kinetic modeling of the different dye

system with an initial concentration of 25 mgL^{-1}.

4.2.6.1 Pseudo first order kinetic model

The linearized form of pseudo-first-order kinetics is given by equation (3.22) in chapter 3 it is clear that, in figure 4.8 a plot of ln (Qe - Qt) Vs. t (time) should give a linear relationship with the slop K_1 and intercept of ln(Qe).

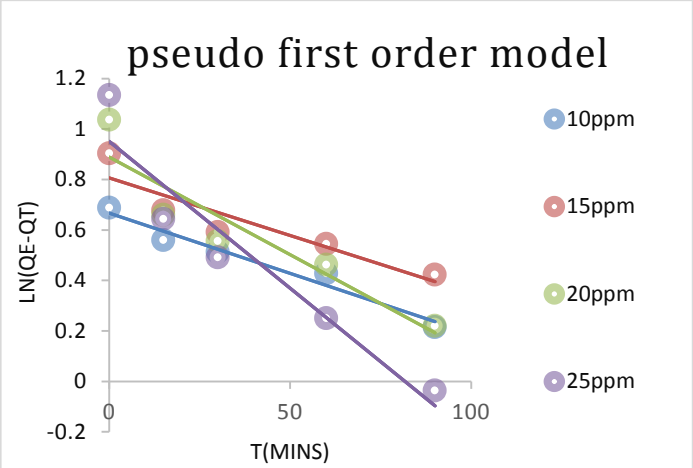


Figure 4.8 Pseudo first order kinetic model for ABC- Safranin system

Table 4.1 Pseudo-first order kinetic constants for the adsorption

C_0 (mg/L)	Qe(exp)	Qe(calculated)	**Forward rate constant K_1 (h^{-1})**	**R^2**
10	4.88	4.646	0.0111	0.9631
15	8.01	6.40	0.0106	0.8439
20	10.89	7.691	0.0177	0.8692
25	13.64	8.923	0.0267	0.9130

4. 2.6.2 Pseudo Second order kinetic model

The linearized form of pseudo-second-order kinetics is given by equation (3.24) in chapter 3. In figure 4.9 a plot t/Q_t Vs of t (time).should give a linear relationship with the slop $1/q_t$ and with intercept of $1/ (K_2.qt^2)$.

Figure 4.9 Pseudo second order kinetic model for ABC-Safranin system

Table 4.2 Pseudo-second order kinetic constants for the adsorption

C_0(PPM)	Qe(exp)	Q_e(calculated)	$k_{L(gm/mg.min)}$	R^2
10	4.88	5.89	0.00317	0.8105
15	8.01	9.83	0.00279	0.8691
20	10.89	11.72	0.00592	0.9804
25	13.64	13.89	0.0117	0.9962

4.2.7 Effect of Temperature

Here the effect of temperature was studies with different temperatures such as 25^0,35^0C, 45^0C and 55^0C. Here experiment were performed at an optimum adsorbent dose = 0.0625g/50 ml of dye solution, pH = 6 and agitation period 120 minutes with 120 rpm [29, 38].

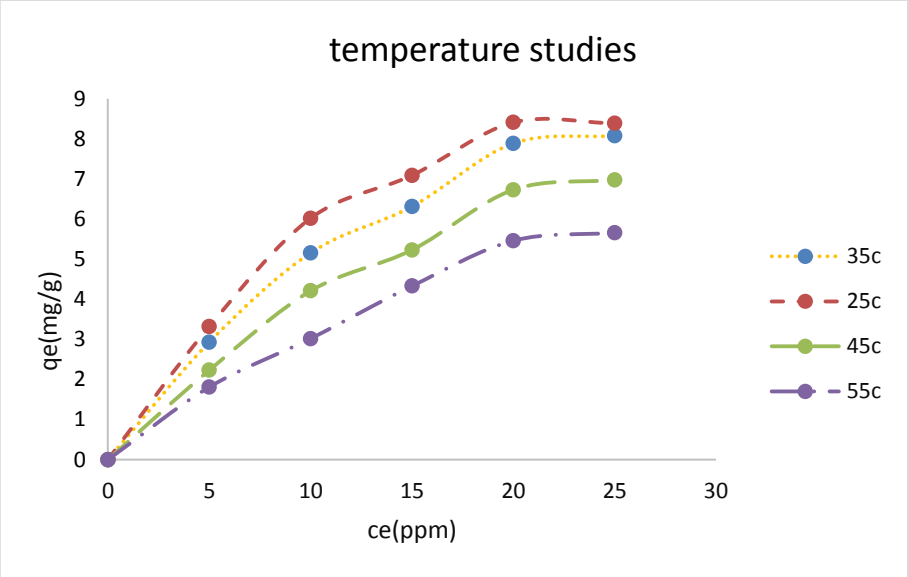


Figure 4.10 Adsorption equilibrium of different temperature for Safranin-ABC system

The temperature studies show that optimum adsorption takes place at 25^0 C. In fig.4.9, the adsorption capacity of dye decreased at higher temperature, which clearly indicates that adsorption of dye in this system, was an exothermic process. For lower temperature the surface coverage increased, may be because of increase of dye penetration inside micro pores at lower temperatures or the creation of new active site as increase surface area. From fig.4.9, it was visualized that adsorption capacity increases with temperature i.e.55^0C < 45^0C < 35^0C < 25^0C.

4.2.8 Adsorption equilibrium study

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. For this equilibrium study of our work, we have considered four basic isotherm models namely Langmuir, Freundlich,

Temkin and D-R isotherm models [29-33, 37].

Adsorption equilibrium study for Safranin – ABC system

4.2.8.1 Langmuir isotherm

The linearized form of Langmuir isotherm is given by equation 3.13 of chapter-3. The Langmuir constant Q_0, and b_L can be calculated by plotting C_e/Qe vs. C_e.

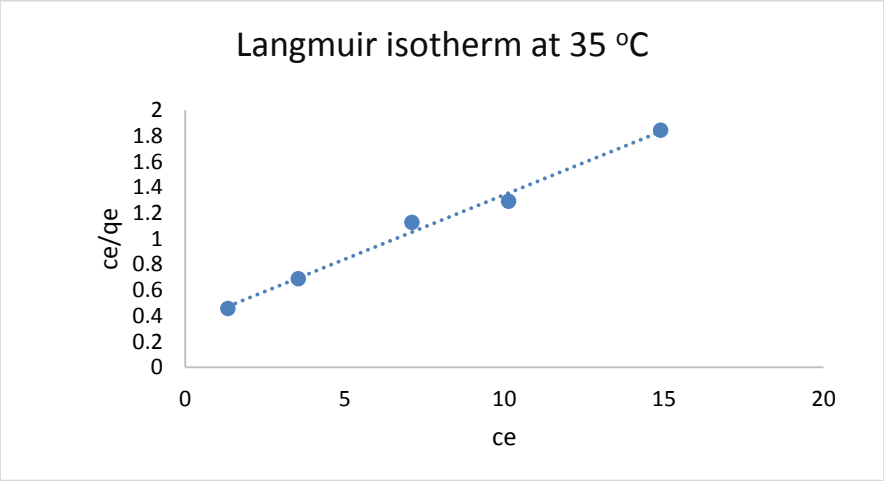


Figure 4.11 Langmuir isotherm for Safranin-ABC system

Similarly In the similar way Langmuir isotherm plots for Safranin-ABC adsorption system at other temperatures were also made and the various parameters calculated from those plots were tabulated below.

Table 4.3 Langmuir isotherm parameters

Temperature(^{0}c)	Qm (mg/g)	b_L(L/g)	R^2
25	9.34	0.162	0.996
35	9.97	0.338	0.991
45	10.55	0.128	0.976
55`	9.104	0.809	0.951

4.2.8.2 Freundlich isortherm.

The linearized form of Freundlich isotherm for Safranin-ABC system is given by equation 3.16 of chapter-3. The value of K_f and n can be calculated by plotting in figure figure 4.12 as ln (Qe) vs ln (Ce).

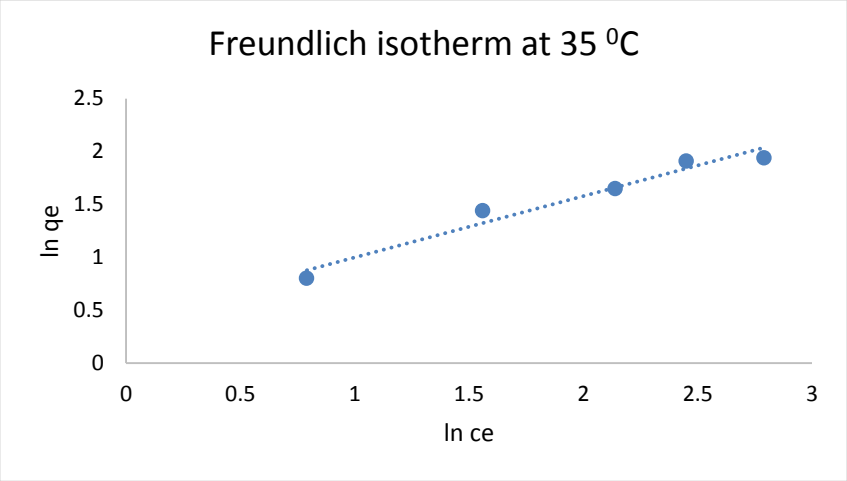


Figure 4.12 Freundlich isotherm for Safranin ABC sytem

Table 4.4 Freundlich isotherm parameters for Safranin-ABC system

Temperature(^{0}c)	K_f	n	R^2
25	3.76	2.94	0.918
35	1.53	1.73	0.961
45	2.73	2.31	0.969
55	0.96	1.55	0.981

4.2.8.3 Temkin Isotherm

The linearized form of Temkin isotherm is given by equation 3.18 of chapter-3. The value of k_T and B can be calculated by plotting in figure 4.13 as Qe Vs ln Ce.

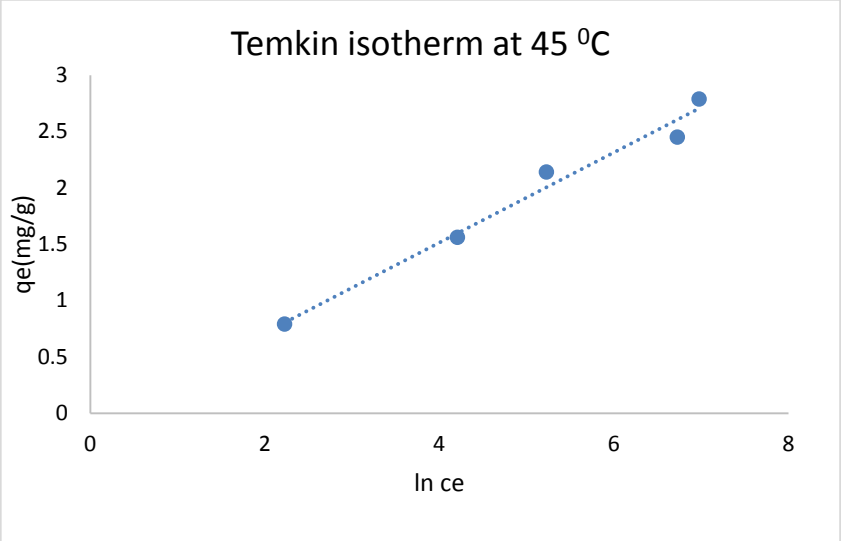


Figure 4.13 Temkin isotherm for Safranin-ABC system

In the below table, Temkin isotherm parameters also calculated with different temperatures for Safranin-ABC system.

Table 4.5 Temkin isotherm parameters for Safranin-ABC systems

Temperature(^{0}c)	B	$k_{T(L/mg)}$	R^2
25	0.5276	0.0222	0.9654
35	0.4431	0.1088	0.9806
45	0.4001	0.8092	0.9795
55	0.4389	2.1389	0.9660

4.2.8.4 D-R Isotherm.

The linearized form of D-R isotherm is given by equation 3.19 of chapter-3. The value of Xm and β can be calculated by plotting in figure 4.14 as Qe vs. Ct.

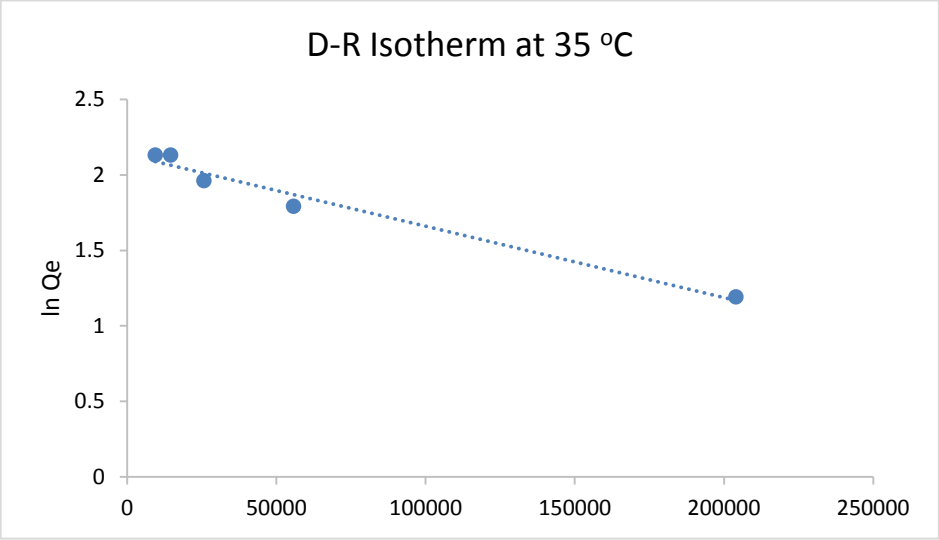


Figure 4.14 D-R isotherm for Safranin-ABC system

In the similar way D-R isotherm plots for Safranin-ABC adsorption systems at other temperatures were also made and the various parameters calculated from those plots were tabulated below.

Table 4.6 D-R isotherm parameter of Safranin-ABC system

Temperature(°c)	β(*10^{-6})	$X_{m(mg/g)}$	R^2
25	5	8.437	0.975
35	5	7.77	0.941
45	5	6.627	0.940
55	5	2.457	0.899

CHAPTER 5

CHARACTERIZATION

5.1 THERMO GRAVITOMETRYANALYSIS (TGA)

Thermo gravimetric Analysis (TGA) relates the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are mainly used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C.This technique can characterize materials that posses weight loss or gain due to decomposition, oxidation, or dehydration [43].

5.2 Fundamental of TGA

TGA study helps us in determining the range of pyrolysis temperature. A sharp bend in the curve shows the temperature at which the pyrolysis has to be started and the temperature at which the curve gets flat shows the end temperature of the pyrolysis. From figure 4, the range of pyrolysis was observed to be from 250 to 550 °C at 10°C/min and 250 to more than 600 °C at 20 °C/min. Initial stage, first stage decomposition represents the evaporation of moisture contents; Second decomposition indicates the formation of volatiles. During the Third stage process, the residue of pyrolysis slowly decomposed, with the weight loss velocity actually becoming smaller and the residue ratio remains to be constant at the end the decomposition of the hydrocarbon. Due to high decomposition rate per unit time, the rapid decomposition zone or Second stage of decomposition is treated as active pyrolytic zone. During this stage, the intermolecular associations and weaker chemical bonds are destroyed. The side aliphatic chains may be broken and some small gaseous molecules are produces because of the higher temperature.

5.2.1 TGA of Blackberry seed.

Here in case of raw blackberry seed, the material kept in temperature about 800 0C.With increases in temperature what is the effect of % mass is measured and calculated the best temperature for pyrolysis. In this graph, we can see that up to the 200 0C, the first stage of decomposition seen.

Again from temperature 200^0C to 400^0C, second stage of decomposition can be seen, which stage of volatile matter removed. Up to 650^0C the third stage of decomposition takes

place. Temperature beyond 6500C mass (%) being constant. Here we can choose the pyrolysis at temperature of 370^0C

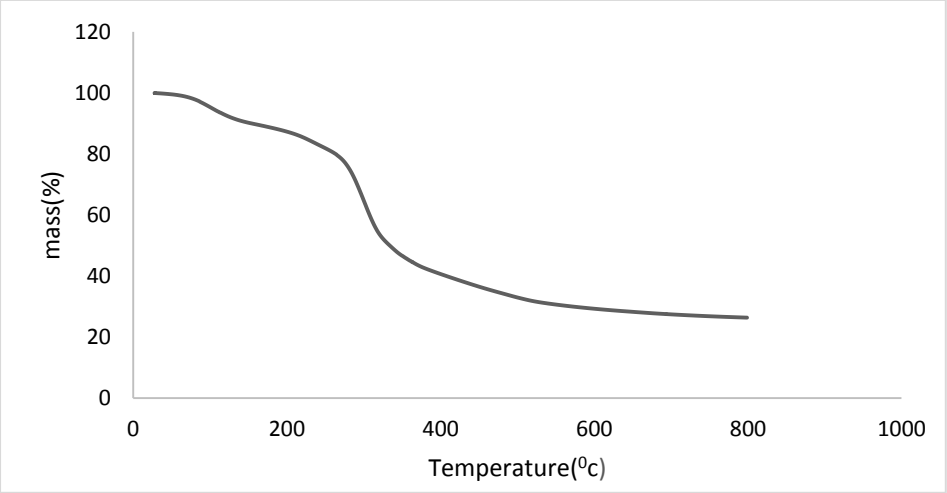


Figure 5.1 Thermogravimetric analysis

5.3 PROXIMATE ANALYSIS

Proximate analysis is one the standard method of physicochemical characterization of the adsorbents. It was developed as a simple means of determining the distribution of products obtained when the coal sample is heated under specific condition. These conditions are strictly according to the ASTM standard of coal heating. As per the definition by ASTM D- 3172 Proximate analysis of coal separates the product into four groups :(i) Moisture, (ii) Volatile matter, consisting of gases and vapour driven off during pyrolysis (iii) Fixed carbon, the non-volatile fraction of coal :and (iv)Ash, the inorganic residue remaining after combustion.

The standard test method for proximate analysis covers the methods of analysis associated with the proximate analysis of the coal and coke and is, in fact, a combination of determination of each of the three of the properties and calculation of the fourth. Moisture, Volatile Matter and ash content are all determined by subjecting the coal to prescribe temperature levels for prescribe time intervals. The losses of weight are, due to loss of moisture and, at the higher temperature, loss of volatile matter. The residue remaining after ignition at the final temperature is called ash. Fixed carbon is the difference of these three values summed and subtracted from 100. In low volatile materials such as coke, the fixed carbon value equates approximate to the elemental carbon content of the sample. Proximate

analysis gives quick and valuable information regarding commercial classification and determination of suitability for particular industrial use.

5.3.1 Moisture Content

Moisture Content generally increases the transportation load and cost and the calorific value reduces**.** 10 grams of char sample taken in a Petridis and kept it in oven at 105-110 ^{o}C for 1.5 hours. Then after the sample taken out and put in the desiccator. After certain time the dried sample weighted and percentage of moisture content was calculated.

5.3.2 Volatile Matter

A known amount of sample was put in a crucible. The crucible was placed in a muffle furnace at 900 ^{o}C ± 10 ^{o}C, covered with lid, and placed for exactly 7 minutes. The crucible was taken out, allowed to cool and weighed.

5.3.3 Ash

The crucible was ignited in the muffle furnace at 650 ± 25 ^{o}C for 1 hour. The crucible was placed in the desiccator, cooled to room temperature and weighed. A known amount of the sample which was dried in the hot air oven at 150 ^{o}C for 3 hours was put in the crucible and the crucible was placed back in the muffle furnace at 650 ± 25 ^{o}C for 3 hours. The crucible was taken out of the furnace, placed in the desiccator, cooled to room temperature and weighed.

5.3.4 Fixed Carbon

Fixed carbon (FC) =100-(volatile matter + ash content+ moisture content).

Table 5.1 Proximate Analysis data (%) (Dry basis)

S.N	Parameters	Blackberry
1	Moisture content %	4.30
2	Volatile matter %	40.18
3	Ash content %	4.31
4	Fixed carbon %	51.2

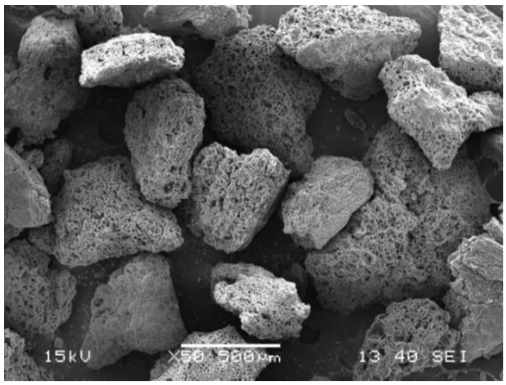
Table 5.2 Ultimate Analysis data (%) (Dry basis)

S.N	Element	Percentage
1.	Nitrogen	1.48
2.	Carbon	63.57
3.	Hydrogen	2.55
4.	Sulphur	1.56

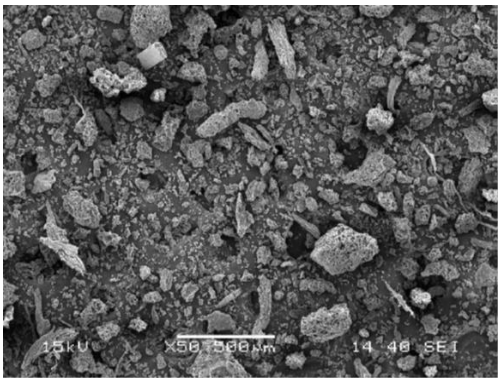
5.4 SEM (Scanning Electron Microscope)

SEM studies stands for scanning electron microscopy, which is used for studying the surface morphology of substances due to its high magnification imaging capability. Scanning electron microscopy images were taken by using JEOL (JSM-6480LV) microscope having an acceleration voltage of 15 kV.

5.4.1 SEM of Blackberry Carbon



(untreated biochar)



(biochar treated with nitric acid)

Investigating SEM, surface morphology, it can be clearly seen that in case of 500X magnification that the surface pores are uniformly distributed. The distribution of pores in activated carbons can vary significant depending upon the raw material. The different shape of pore with different of raw material. The pore size distribution also affects the efficiency and selectivity of adsorption. A consideration of the dimensions of some pollutants shows that activated carbon can feasibly be used to remove many of the impurities occurring in water.

5.5 BET ANALYSIS

In case of gas adsorption, both the Adsorption and desorption at any clean surface of dry solid powder as well as the pore size distribution of pours materials. In an experiment of gas sorption, the material is being heated and degassed by vacuum force or inert gas, such as N2,krypton or alternatively withdrawn and desorbed. The sample materials is placed in a vacuum chamber at a very low constant temperature, generally at the temperature of liquid nitrogen (77.4 K) and it operated at a wide range of pressure for generating adsorption and desorption isotherms. The amounts of gas molecules adsorbed or desorbed are determined by the pressure variations due to adsorption and desorption of the gas molecules by adsorbent.

Table 5.3: BET analysis data of activated blackberry carbon (ABC)

Name of Material / adsorbent	Adsorbent External surface area, m^2/g
Activated blackberry carbon	229.9

Various amount of gas molecules will be adsorbed or desorbed at different doses of the gas (the adsorbate).Total surface area of the material can be determined by knowing the area occupancy of a single adsorbate. Both single point and double point method is used to find the surface area. Most widely used method of determining the surface area is BET nitrogen adsorption method. The multipoint as 5 points, 10 points, 20 points and etc. can be calculated. BET method is used to measure total surface area.

5.6 Fourier Transform Infra-Red spectroscopy (FTIR)

Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique that detects various characteristic functional groups available in any solid or liquid sample. Basically it is a spectroscopic analysis technique which is used for identification of chemical bonds in a molecule by producing an infrared absorption spectrum and from there of the functional groups present on the surface of sample. Interaction of an infrared light with Activated carbon the chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range in the presence of the rest of molecules. Based on this, the principle functional groups present in the activated biomass carbon were identified. During

analysis the sample is irradiated by infrared radiations, some of the infrared radiations are absorbed by the sample and rest are passed (transmitted) through. The FTIR spectra were collected generally in the range of 400-4000 cm-1 region with 8cm-1 resolution. Absorption in the infrared region makes changes in vibrational and rotational status of the molecules. The absorption frequency depends greatly on the vibrational frequency of the molecules. The absorption intensity depends on how the infrared photon energy can be transferred to the molecule. This depends on the change in the dipole moment that occurs as a result of molecular vibration. A molecule will absorb infrared light only if the absorption causes a change in the dipole moment.

This spectrum represents a fingerprint of the sample with absorption peaks corresponding to the frequencies of vibrations between the bonds of the atoms which make up the material. Thus, it gives an idea about the organic functional groups present in the sample. The samples were usually prepared with KBr, in the form of pellets. FTIR analysis is done using the instrument FTIR analyzer by Shimadzu IR Prestige-21, Manufacture in Japan.

FTIR analysis of Virgin ABC and dye loaded ABC

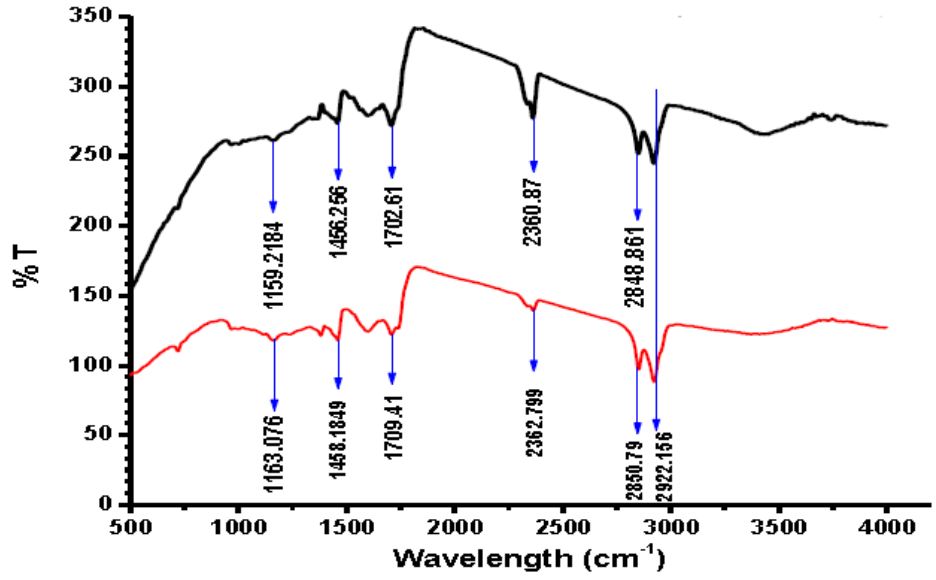


Figure 5.2 FTIR analysis of virgin and dye loaded ABC

Region between 3200-2700 cm-1 indicates for organics and hydrocarbon, in this region are normally characteristics of carbon and hydrogen containing species which are assigned to various forms of C-H stretching. Peak no.2922.156 cm-1 Characteristic of carbon-and hydrogen containing species, with single bond and are assigned to various forms of C-H stretching, CH3, Alkane. It can be inferred that the alkane group do not play any significant role in adsorption, means peak remain unchanged. Peak 2848.861 cm-1, characteristic of carbon-and hydrogen containing species, with double bond and are assigned to various forms of C-H stretching ,CH2, Alkene. After Safranin dye adsorption peak shifted to 2850.79cm-1. Peak 2360.87cm-1, characteristic of carbon-and hydrogen containing species, with single bond and are assigned to various forms of C-H stretching, dye loaded AMC shifted to 2362.87. Peak no.-1702.61cm-1 characteristic of carbon and oxygen containing species and are assigned to various forms of C double bond with oxygen stretching ,=C=O group(carboxylic group) and after loading of dye it shifted to 1709.41cm-1. Peak no.-1456.25 cm-1, characteristics of methane bending and are assigned to form of C-H bending, CH2 group, after dye loading shifted to 1458.18 cm-1. The presences of these groups are responsible for adsorption of Safranin dye on to the Activated blackberry seed carbon, ABC (adsorbent) surface.

CONCLUSION

CONCLUSION

Removal of Safranin (Safranin O) dye from aqueous solutions by adsorption using activated carbon prepared from *Syzygium cumini* (activated jamun seed carbon) was experimentally determined. The prepared activated carbon was characterized by different analysis and test.

For my whole project work, activated blackberry seed carbon (ABC) chosen for adsorption studies because of its high BET surface area along with other characterization analysis.

For Safranin-ABC system:

- Chemical activation of precursor by nitric acid with impregnation ratio (1:5) solid liquid ratio gave better adsorbent surface morphology nature.
- BET Surface area as a characterization parameter of ABC confirmed the mesoporous texture, highly carbonaceous nature and a higher effective multi-layer adsorption using N2 as surface area of 229.9 m^2/g.
- Point Zero charge (pH_{pzc}), of ABC was determined as 6.0. At this pH the adsorbent surface's net charge become zero.
- The maximum adsorption capacity of dye was found to 36.6.152 mg/g.
- For Safranin-ABC system optimum adsorbent dose, M= 1.25 g/L, t= 2 hours as sufficient time for maximum removal and mixing of dispersed solution.
- As pH is a most influencing parameter and pH=6.2 set as optimum value, adsorption for this system took place in mildly acidic environment.
- Increasing of time give a consecutive higher value uptake capacity up to a certain period and then became constant at time equals 120 min. Uptake capacity increase with increase of initial dye concentration. Maximum uptake capacity was found at initial adsorbate concentration equals to 25 PPM.
- At Temperature 25^0C maximum dye removal took place and kept on decreasing on increasing the temperature suggesting the exothermic nature of adsorption.
- In case of Safranin-ABC, maximum removal was achieved with having operation variable as followed, pH = 6.2, adsorbent dose 1.25 g/L, C0 = 25 mg/L, V=50 ml, optimum contact time was 120 minutes with 120 rpm of shaker and temperature at 25^0C.

- The kinetic of adsorption followed the pseudo second order kinetic model.
- For best fitting to adsorption isotherms, the values of it compared with linearity by R^2 value, which showed as, Langmuir isotherm> freundlich > Temkin > D-R isotherm.

FUTURE WORK

The following recommendation to be done for further studies:

- Adsorption studies of Safranin (basic dye) using other self-prepared or commercial adsorbents.
- More detail characterization of self-prepared adsorbents must be performed.
- Optimization of process/operation variables using statistical method.
- Adsorption studies will investigate through the *continuous flow system* method and fluidized bed system also be performed for best utilization of this adsorption process.
- Safranin dye desorption studies will also be performed.

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